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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.028
 wR factor = 0.075
Data-to-parameter ratio = 16.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

3-Bromomethyl-5-chloro-2-benzothiophene

The title compound, $\text{C}_9\text{H}_6\text{BrClS}$, was synthesized in a search for new benzothiophene compounds with potentially high bioactivity. In the crystal packing, a weak $\text{Br}\cdots\text{Cl}$ interaction is present.

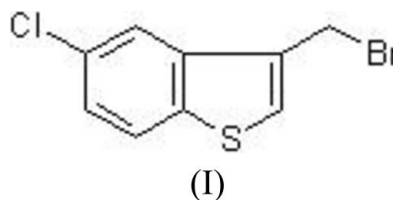
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Comment

Benzo[*b*]thiophene derivatives have attracted much interest in organic chemistry (Bianchini & Meli, 1997; Cabiddu *et al.*, 2002) because of their pharmacological activities and chemical properties. They display antibiotic, analgesic, anti-exudative, anti-inflammatory and diuretic activities, and are widely used in the synthesis of thioindigo dyes. In a search for new benzothiophene compounds with potentially high bioactivity, we have synthesized the title compound, (I), and report its crystal structure here.



The molecular structure of (I) is shown in Fig. 1. The benzothiophene ring system is planar, the maximum deviation from planarity being 0.012 (3) Å for atom C7. Bond lengths

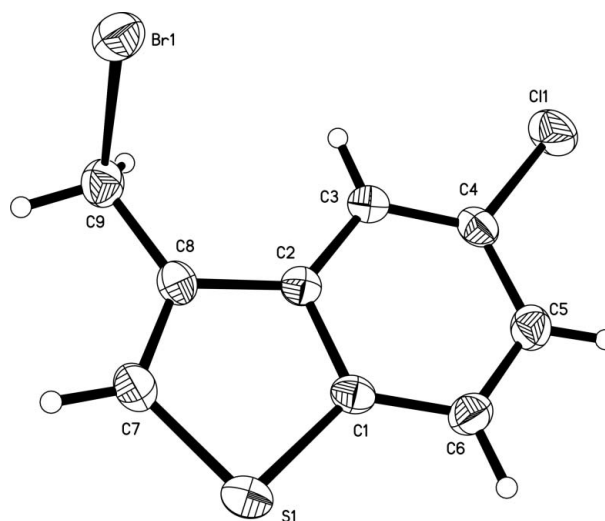


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

and angles (Table 1) are within expected ranges, with the C—S bonds averaging 1.726 (3) Å.

In the crystal packing (Fig. 2), a weak Br⋯Cl contact [Br1⋯Cl1ⁱ 3.683 (1) Å; symmetry code: (i) 1 - x, -½ + y, ½ - z] is observed. No significant hydrogen-bonding or π-π interactions are present.

Experimental

The title compound was prepared according to the method described by Cabiddu *et al.* (2002). 4-Chlorothiophene (10 mmol) and KOH (11 mmol) were dissolved in EtOH (5 ml) and H₂O (5 ml) at room temperature, then BrCH₂COCH₃ (10 mmol) and ethyl acetate (20 ml) were added dropwise. The mixture was stirred magnetically for 2 h and the resulting white solid product, (4-chlorophenylthio)acetone, was purified by preparative thin-layer chromatography on silica gel with cyclohexane and ethyl acetate (10:1) as eluent. Polyphosphoric acid (PPA, 2.5 mmol) and (4-chlorophenylthio)acetone (3 mmol) were added to dimethylbenzene (5 ml) under a nitrogen atmosphere. The mixture was refluxed for 1 h to give 5-chloro-3-methylthianaphthene. The title compound was prepared by reaction of *N*-bromosuccinimide (3 mmol) with 5-chloro-3-methylthianaphthene (2 mmol) at 393 K for 3 h, and purified by column chromatography (hexane-EtOAc, 5:1) (yield 85%) (Nandi *et al.*, 2002; Hessian & Flynn, 2003). Single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation at 298 K of a 4:1 (v/v) ethyl acetate-petroleum ether solution. Spectroscopic analysis: IR (KBr, ν, cm⁻¹): 3008, 2898, 1780, 1080, 817; ¹H NMR (CDCl₃, δ, p.p.m.): 7.63 (*m*, 2H), 7.26 (*m*, 2H), 4.82 (*s*, 2H).

Crystal data

C ₉ H ₆ BrClS	$D_x = 1.867 \text{ Mg m}^{-3}$
$M_r = 261.56$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3579 reflections
$a = 7.2891 (9) \text{ \AA}$	$\theta = 1.9\text{--}25.3^\circ$
$b = 13.6044 (16) \text{ \AA}$	$\mu = 4.86 \text{ mm}^{-1}$
$c = 9.4539 (12) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\beta = 96.946 (2)^\circ$	Prism, colourless
$V = 930.6 (2) \text{ \AA}^3$	$0.28 \times 0.20 \times 0.13 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	1823 independent reflections
φ and ω scans	1566 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$R_{\text{int}} = 0.016$
$T_{\text{min}} = 0.325$, $T_{\text{max}} = 0.530$	$\theta_{\text{max}} = 26.0^\circ$
5138 measured reflections	$h = -8 \rightarrow 8$
	$k = -16 \rightarrow 14$
	$l = -9 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.2265P]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.075$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
1823 reflections	$\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$
109 parameters	
H-atom parameters constrained	

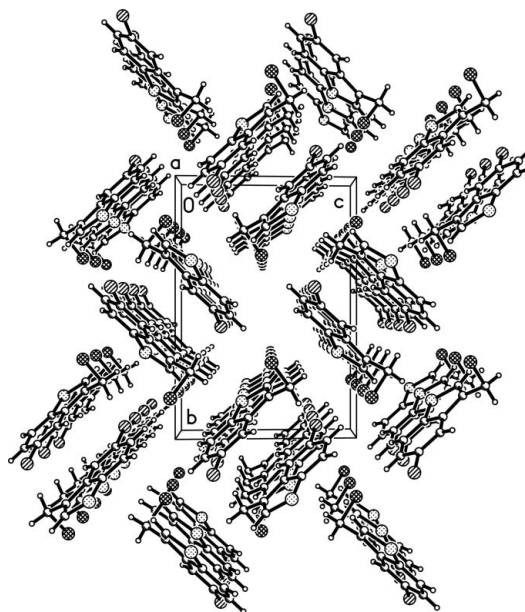


Figure 2

A packing diagram of compound (I), viewed down the *a* axis.

Table 1

Selected geometric parameters (Å, °).

S1—C7	1.719 (3)	C2—C8	1.440 (3)
S1—C1	1.734 (2)	C7—C8	1.349 (4)
C1—C2	1.416 (3)		
C7—S1—C1	90.97 (12)	C8—C7—S1	114.5 (2)
C2—C1—S1	111.16 (18)	C7—C8—C2	111.7 (2)
C1—C2—C8	111.6 (2)		

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.95–1.00 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Bruker, 2002); software used to prepare material for publication: SHELXL97.

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References

- Bianchini, C. & Meli, A. (1997). *Synlett*, pp. 643–649.
- Bruker (2002). SMART, SAINT, SADABS and XP. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cabiddu, M. G., Cabiddu, S., Cadoni, E., Demontis, S., Fattuoni, C. & Melis, S. (2002). *Tetrahedron*, **58**, 4529–4533.
- Hessian, K. O. & Flynn, B. L. (2003). *Org. Lett.* **5**, 4377–4380.
- Nandi, S., Syam Kumar, U. K., Ila, H. & Junjapp, H. (2002). *J. Org. Chem.* **67**, 4916–4923.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.